ELECTROPHORETIC NANO-COATING

FIELD OF THE INVENTION

The present invention is related to the deposition of polymer coatings on conductive substrates, for instance substrates made of iron or other metals and their alloys such as aluminum and Mg alloys, or for the formation of decorative layers to be used in the toy industry, corrosion protection and decoration for metal frames and furniture, and for protecting imitation jewelry and metallic spectacle frames.

BACKGROUND OF THE INVENTION

The traditional technology employed to achieve corrosion protection for metals often employs the use of organic polymer coatings such as paints and lacquers. Electrophoretic technology has been shown to produce excellent organic coatings with desirable performance characteristics and has been a widely used technology by various industries, such as for coating of agricultural equipment, appliances, automobiles, automotive parts, marine components, metal office furniture, lawn & garden equipment, furniture and other industrial metallic subjects for more than 30 years. It has evolved dramatically and new end uses for electrocoating are found annually.

Due to the recent increasing concern for environmental protection, and for public health and safety, numerous water-based systems have been developed

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to replace the organic solvent based systems in the surface finishing industry. However, the coating quality for the water-based system is in general inferior to that of the organic solvent based systems. The nano-sized polymer emulsions developed in recent years provide a breakthrough in this area, as its improved coating quality with desirable properties has led to promising market potentials, particularly where regulations for the reduction of organic solvent have been imposed on the architectural coating industry. For instance, a road map has been drawn in China and Hong Kong to regulate the emission of organic vapour during industrial processes.

Polymer emulsions have been used commercially for many years in electrocoating. A number of patents exist describing the use of a polymer emulsion in an electrocoating process. However, the particle size for the emulsions is often not stated and if stated, is generally either outside the nano-size range (up to 100 nm) or encompasses a wide range which is mostly larger than nano-size. For example, the particle size in the emulsion described in Graun et al, U.S. Pat. No. 4,608,139 (Aug. 26,1986) is from 40 to 1000 nm, preferably 150 to 600 nm, so that the average particle size is outside the nano-range. The emulsion in Abbey et al U.S. Pat. 4,511,446 (Apr. 16,1985) uses an average particle size not substantially smaller than 100 nm while mentioning a size as low as 30 nm is possible. Another undesirable characteristic of the emulsion used is the use of a large amount of organic co-solvent that cause environmental and safety concerns. For example, the emulsion in Chung et al U.S. Pat. No. 5,185,065 issued Feb. 9,1993, Abbey et al U.S. Pat, 4,511,446 issued Apr. 16,1985, Dudley U.S. Pat. No. 4,136,074 issued Jan. 23,1979, and Kolish et al U.S. Pat. 3,978,015 issued Aug 31, 1976,

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always contain alcohol or other organic co-solvents and surfactants.

SUMMARY OF THE INVENTION

The nano-emulsions of the present invention contain nano-particles in a very narrow particle size distribution of between 10 and 100 nm, and with a great reduction in the use of organic co-solvent, generally to less than about 1%. In addition to the fact that these nano-emulsions are environmental friendly, the coatings produced by them also show improved properties due to a suitable interaction between the deposited nano-particles to produce a much thinner, transparent and non-porous coating with excellent corrosion protection. When used as a binding material in the electrocoating process, the nano-emulsion has shown to produce coatings with excellent stability, low permeability, good soaking ability and fluidity because of the small size of the nano-particles. This enables their penetration into ultra-small holes, indentation and capillary areas at surface of the metallic subject. This is especially advantageous in coating very complex shapes to give high quality homogeneous coatings. The formation of thin or ultrathin films of several nanometers thickness (e.g., about 10 to several micrometers) creates a highly transparent layer that can not be detected by touch or visually with the unaided eye. Thus, they are particular desirable for decorative purpose for imitation jewelry. During co-deposition with other pigment particles, the nano-sized particles can penetrate into the gap between larger particles. Thus, the hardness, coherence, smoothness and brightness of the pigment-containing coating can be greatly improved. The use of nano-emulsions can reduce the occurrence of electrophoretic separation of pigments, lessen the formation of cracks and produce special colour-coatings with customer appeal that have a high potential for future market development.

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The electrophoretic nano-coating technology described in this invention is a combination of an electrophoretic process with a polymer nano-emulsion or a pigment-containing nano-emulsion. The use of a polymer emulsion with particle sizes in the nanometric range for electrophoretic painting is new. The combination of using a good throwing power of the electrophoretic process and a polymer nano-emulsion to deposit a non-porous and dense polymer nanocoating produces most desirable coatings. It broadens the application of polymer nano-emulsion for functional and decorative coatings. Firstly, it allows new areas of application such as protective top-coating for light metals and their alloys such as aluminum and Mg alloys. Secondly, deposition to form decorative layers with customer appeal will extend its application in the toy industry, extended uses in corrosion protection and decoration for metal frames and furniture, and for protecting imitated jewelries and metallic spectacle frames.

A conductive substrate is immersed in a water-based electrophoretic nano-emulsion, and an electric current is then passed through both the metallic substrate and the emulsion. The charged nano-particles are moved by the electric field toward the substrate with other paint particles present and adhered to the substrate surface to build up an electrically insulating coating layer. This coating covers the entire metallic substrate and is self regulating in that the insulating layer formed prevents subsequently applied electric current to pass through the system, resulting in a very uniform coating even in the recess areas of complex-shaped items. After the substrate is coated, it can be cured in an oven to allow the nano-polymer particles to flow and cross-link with each other. This provides the coating formed with excellent protective and decorative

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properties that are desirable for many industrial applications.

DETAILED DESCRIPTION OF THE INVENTION

The nano-emulsion of this invention is a water-based polymer emulsion containing nano-size particles, i.e., up to 100 nm, preferably between 10 to 100 nm. The emulsion commonly contains emulsified particles of a water-dispersible acrylic or modified acrylic polymer, although other water-dispersible polymers such as polyurethanes can be used. A number of such polymer emulsions are now commercially available with a solid content between about 40 to 60%. Confirmation of a nano-size range in an emulsion asserted to be a nano-emulsion can be determined by use of an atomic force microscope or a transition electron microscope.

The nano-emulsion contains water with emulsified nano-sized particles of ionic polymer together with other customary electrophoretic additives. Such additives can include emulsifier(s), defoaming agents, leveling agents, drying agents, thickeners and thixotropic agents, fillers, antiseptics, and the like. All of such additives are commercially available. For example, T-731 dispersant and TT-935 thickener are supplied by Rohm and Hass Company, 5040 dispersant and NXZ defoamer by Henkel Company, and EFKA 3580 leveling agent and defoamer 2526 by EFKA Additives. Organic solvent should be essentially absent (i.e., less than about 1%).

When a transparent coating is desired, a pigment-free nanoemulsion is

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prepared. Firstly, a commercially available polymer nanoemulsion is diluted with water, preferably distilled water, to adjust the solid content of the emulsion to an appropriate deposition concentration. This can be about 10~20%, although other concentrations can be employed if desired. In order to achieve a satisfactory coating during the electrophoric process, the conductivity of water must be controlled to below 5µS/cm. This is achieved by appropriate selection of the emulsion constituents. Likewise, the pH of the emulsion is adjusted to be basic in order to control the charge on the polymer particles and regulate the deposition process. Preferably, the pH range is from 7.8 to 9.0 and this is achieved by employing a suitable base in the emulsion, such as, for instance, 2-amino-2-methyl-1-propanol (AMP-95), N,N-dimethylethanolamine or triethylamine. To obtain a quality coating, the emulsions having the appropriate solids concentration, conductivity and pH must be matured (equilibrated) before use by, for instance, stirring for an extended period of time. Maturing time, temperature and stirring rate are interdependent in that increasing one permits greater latitude in selecting the other parameters to be employed. A suitable maturing procedure can involve a stirring rate of 1500 revolutions per minute under ambient conditions for at least 48 hours in a cell made up of PP plates.

Standard electrophoretic coating procedures can be used in the present invention. Typically, the conductive substrates to be coated are degreased in an ultrasonic bath containing a detergent for 20 minutes at a constant temperature of 30°C. Then the substrates are rinsed with tap water and pure water before being immersed in the matured nanoemulsion using a suitable holder. Under stirring at room temperature, a driving voltage of, for instance,

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between 15 to 30 V, is imposed between the conductive substrate and a counter electrode of, for example, steel, for about 15 ~ 60 seconds. After removal from the electrophoric cell, the coated substrates are rinsed, for instance in tap water and then pure water for at least two minutes respectively, to remove any uncoated emulsion. The rinsed work-piece should be dried, for example in air for at least 10 minutes, until no water is visible at its surface before placing it into an oven for baking. The work-pieces are cured at a constant temperature of about 100 to 180° for about 20 to 30 minutes. An optically transparent coat is obtained. The films thus obtained consist of pure polymer coating and are free from pigment particles.

Alternatively, nanocomposite coatings which are pigment-containing coatings electrodeposited from the nanoemulsion bath can be realized. In this case, electrodepositable pigment particles are codeposited with the nanoparticles during the electrophoretic process. Due to the strong binding of the nano-sized emulsion particles with the pigment particles, the nanocomposite coatings possess excellent corrosion protection and show other desirable properties.

A typical procedure for the preparation of a pigment-containing nano-emulsion bath can as follows:

(1) Appropriate amounts, e.g., weight parts, of pure water, dispersant, defoamer, antiseptic, and leveling agent in light of the desired formulation and a quantity of pH adjuster are added to a container and well mixed under a high stirring speed using a dispersing machine.

(2) A quantity of commercially available nano-emulsion to provide one-half of the desired nano-particle content is added into the container and mixed well.

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(3) Selected amounts of pigments and fillers are added into the container and mixed well.

(4) The mixture thus obtained is then transferred into a mill for grinding.

(5) The paste obtained by grinding is transferred to a container, following by the addition of the remaining amount of nano-emulsion.

(6) Drying agent, thickener and pH adjuster are added to the container and mixed well with the above paste.

(7) Finally, a pigment-containing nano-emulsion bath is obtained by the addition of pure water and pH adjuster to the paste to adjust the solid content and pH value to within 10~20% and 7.8~9.0, respectively.

This nano-emulsion bath contains pigments and additives. The pigment in this nano-emulsion can be any of the pigmented compositions commonly used in the coatings industry for electrophoretic applications, for example, those commercially available such as iron black and carbon black for primer coatings. The preferred range of pigment in emulsion is from about 1 to 30 wt%. The pH adjuster is preferably 2-amino-2-methyl-1-propanol (AMP-95). The conductivity of pure water is controlled to under $5\mu S/cm$. A typical formulation for a nano-emulsion bath is given below:

Constituents	Weight percent, %
Nano-emulsion	50~80
Pigment and filler	1~30
Dispersant	0.1~0.5
Thickener	0.2~5
Drying agent	1~4

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pH adjuster   0.1~0.5

Defoamer   0.01~0.05

Pure water   5~10

The coating is typically conducted in the pigment-containing nano-emulsion bath on conductive substrates after the work-pieces are degreased in an ultrasonic bath containing detergent for say 20 minutes at a constant temperature of 30°. For the production of a composite coating using the electrophoretic process, the conductive substrates are immersed in the waterborne nano-emulsion in an electrophoretic cell of, e.g., polypropylene, under the application of a driving voltage. After the substrates are coated, they are rinsed by tap water and then pure water for at least two minutes, respectively, after removal from the PP cell. The rinsed work-pieces are dried in air for at least 10 minutes until no water is visible at the surface of the work-piece before being put into an oven for baking. The resulting nanocomposite coating can be a primer coating or a top coating. Typical operation ranges for the working parameters of the electrophoretic and baking process are summarized in Table 1.

Table 1

Working parameters	Operation ranges
Voltage /V	15 ~ 30
Electrophoretic time /s	15~ 60
Bath temperature C°	20~30

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Baking temperature /C°	100~180
Baking time /minutes	20~30

In order to further illustrate the present invention, various non-limiting examples are set forth below.

Example 1 - Transparent polymer nanocoating

An acrylic polymer nano-emulsion labeled ZBE 612 was obtained from Tsingdao Ocean Chemical Institute. The average polymer particle size in this nano-emulsion is around 50 nm. As supplied, the solid content and pH value are 40.2% and 7.8, respectively. Two parts of pure water was mixed with one part of the nano-emulsion in an electrophoretic cell made up of PP plates. The pH value of the nano-emulsion was adjusted to 8.2±0.3 by addition of base. The emulsion obtained was matured by stirring under ambient condition for 48 hours. An electrophoretic process was then conducted on a variety of conductive work-pieces (steel, iron, copper, and their aluminum and Mg alloys). Finally, transparent polymer nanocoatings were obtained after baking of the work-pieces. The optimized working parameters for the production of transparent nanocoatings using this emulsion and the performance of the resulting coating are listed in Table 2.

Table 2. Working Parameters and Performance

Working parameters	Operation ranges
pH	8.2±0.3

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Conductivity /μS·cm^{-1}	800~1200
Solid content / %	10~18
Voltage /V	15~30
Electrophoretic time / s	15~60
Bath temperature /°C	22~25
Baking temperature /°C	120
Baking time /minutes	30
Appearance of coating	Optically transparent, smooth thin film
Coating thickness /μm	5~20
Hardness (BS 3900-E1:2002)	2~3H
Adherence	1
Resistance in 3% NaCl solution	>240 hours(25°C)
Bend Test (Cylindrical mandrel)	5mm diameter rod, bend 180° (pass)
Resistance to acid	1% H_2SO_4 280 hours (pass)
Resistance to weathering	Outdoor exposure for 30 days (did not change to yellow)

Example 2 - Black composite primer nanocoating

A nano-sized emulsion labeled ZBE611 with an average particle size of 50 nm was obtained from Tsingdao Ocean Chemical Institute. Two composite pigment-containing nano-emulsions A and B were prepared according to the formulations given in Table 3. Electrophoretic coating of variety of conductive work-pieces (steel, iron, copper, and their aluminum and Mg alloys) was

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effected using the A and B composite nano-emulsion, respectively. Black composite nanocoatings were obtained after the baking of the work-pieces. The optimized operation ranges for the coating procedure and performance evaluations are listed in Table 4.

Table 3. Compositions of the composite nano-emulsion of A and B.

Constituents	Weight percent (%), A	Weight percent (%), B
ZBE 611 nano-emulsion	83	79
Dispersant agent	2	2
AMP-95	0.3	0.3
defoaming agent	0.3	0.3
Carbon black	3	3
Gas-deposited SiO_2	1	1
717 resin	-	9
Drying agent	5	0
Leveling agent	0.2	0.2
Thickener	2.0	2.0
Pure water	3.2	3.2

Table 4. Optimized operation ranges for the black composite nanocoatings and their performances

Working parameters	Operation ranges, A	Operation ranges, B
pH	7.8~8.2	7.8~8.2

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Conductivity /$\mu S \cdot cm^{-1}$	800~1300	800~1300
Solid content / %	10~18	10~18
Voltage /V	15~30	15~30
Electrophoretic time / s	15~60	15~60
Bath temperature /°C	22~25	22~25
Baking temperature /°C	120	120
Baking time /minutes	30	30
Appearance of coating	Black, compact	Black, compact
Coating thickness, μm	10 ~80	10~80
Hardness	2H	3H
Adherence	1	1
3% NaCl solution (25°C), hours	>240	>480
Bend Test (Cylindrical mandrel)	5mm diameter rod, bend 180 degree (pass)	5mm diameter rod, bend 180 degree (pass)
Resistance to acid	1% H_2SO_4 240 hours (pass)	1% H_2SO_4 480 hours (pass)

Example 3 - Golden decorative nanocoatings

An acrylic polymer nano-emulsion labeled ZBE 612 and a golden color paste in a concentration of 55~65 ml/L were mixed in a cell made up of PP plates. A golden nano-emulsion was obtained after the golden color paste was dispersed well by stirring. The average polymer particle size in the ZBE 612

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nano-emulsion is around 50 nm. The solid content and pH value of the nano-emulsion as supplied are 40.2% and 7.8, respectively. Two parts of pure water was mixed with one part of the golden nano-emulsion in the electrophoretic cell. The pH value of the nano-emulsion was adjusted to 8.2±0.3. The diluted golden nano-emulsion was matured by stirring under ambient condition for 48 hours. An electrophoretic process was then conducted using a variety of conductive work-pieces (steel, iron, copper, and their aluminum and Mg alloys). Finally, golden polymer nanocoatings were obtained after baking of the work-pieces. The optimized working parameters for this emulsion and its operation ranges for the production of golden nanocoatings were listed in Table 5.

Table 5. Optimized working parameters for the production of golden nanocoatings and their performances

Working parameters	Operation ranges
pH	8.2±0.3
Conductivity /$\mu S \cdot cm^{-1}$	800~1200
Solid content / %	10~18
Voltage /V	15~30
Electrophoretic time / s	15~60
Bath temperature /°C	22~25
Baking temperature /°C	120
Baking time /minutes	30
Appearance of coating	Smooth, golden compact thin film
Coating thickness /μm	5~30

Hardness	2~3H
Adherence	1
Resistance in 3% NaCl solution (25°C)	>360 hours
Bend Test (Cylindrical mandrel)	5mm diameter rod, bend 180 degree (pass)
Resistance to acid	1% H_2SO_4 480 hours (pass)
Resistance to weathering	Outdoor exposure for 30 days (do not change to yellow)

Various changes and modification can be made in the process and products of this invention without departing from the spirit and scope thereof. The various embodiments described herein were for the purpose of further illustrating the invention and were not intended to limit it.